Sorption of Hydrogen Cyanide by Mature Lemons and Oranges in a Dynamic System and in a Commercial Fumatorium as Evaluated by Gas Chromatography with Nitrogen Detector

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Sorption of gaseous HCN by unwaxed and waxed lemons and oranges was evaluated in all-glass apparatus and in a commercial fumatorium, with gas chromatography with nitrogen detector to determine nonsorbed and desorbed HCN. Fruits were fumigated with 6 to 128 mg of HCN/l. for 1-hr periods at 30° and 43° C, in light and in dark. Although 6 mg/l. is the concentration required by law, excessive amounts were also used for following desorption processes and conditions, and to simulate commercial conditions near the point of HCN introduction. In the laboratory quick sorption by waxed or unwaxed fruits occurs almost immediately, with sorption of 70 to 94% of the initial amount. In the fumatorium, 83 to 84% is sorbed within 30 min by waxed lemons and oranges. HCN previously sorbed desorbs only 3 to 7% after 10 min aeration. Final HCN residues in fruits range from 21 to 572 ppm, depending upon dosage and duration of exposure.

The first important field use of HCN as a fumigant was in California in 1886 for controlling scale insects on citrus trees, with injection of the gas under a canvas sheet or tent covering the tree. It has been used widely for more than 70 years in most of the citrus growing regions of the world, and is still in use in some of them. An estimated 50,000 to 60,000 acres of citrus trees were fumigated annually with this gas for many years in California (Lindgren and Vincent, 1966).

Fumigation today is one of the most important methods of controlling insects in stored products and in the sterilization of infested commodities moving into noninfested areas. Many goods imported into a country or area have to be treated in such a way as to destroy completely potentially dangerous insects, and thus prevent their introduction into that country or area. HCN is still used for this purpose and also for citrus fruits shipped into Arizona. Japan and several other countries require HCN treatment of imported citrus fruits. The water solubility of HCN limits its use on moist materials such as many vegetables and most fruits other than citrus, because in contact with moist commodities it usually causes burning, discoloration, wilting, and flavor changes, thus rendering the commodities unmarketable.

There is little information on the sorption of HCN by foodstuffs. Moore and Willaman (1917) reported from 0.003 to 0.01% of HCN in dry weight of HCN-fumigated tomatoes. Bartholomew *et al.* (1939, 1942) have studied the sorption and desorption of HCN by both green (almost fully sized) and mature Valencia oranges, using a nonspecific titration technique. They found these fruits quickly sorbed gaseous HCN, even into internal (pulp) tissues, and that 4 hr after fumigation for 40 min at 75° F with 6 mg of HCN/l. of air, 38–48% of the sorbed HCN was not recoverable by aeration or even by a drastic distillation technique. After 48 hr, from 72 to 85% of the sorbed HCN was fixed in the orange tissues. Furthermore, they demonstrated that in closed containers all the HCN initially absorbed by these fruits was eventually irreversibly sorbed (fixed) by the fruit tissues. Green oranges (4.5 cm diam) absorbed about five times more HCN per unit fruit surface than did mature fruits (7 cm diam). There were no differences between HCN recoveries from day-fumigated *vs.* night-fumigated fruits in the field.

The present study reports a quantitative and rate evaluation of the HCN sorbed by both waxed and unwaxed mature Eureka lemons and navel oranges during fumigation and desorbed after fumigation, as evaluated by gas chromatography with a specific nitrogen detector. The results obtained confirm and expand the conclusions of Bartholomew *et al.* (1942). The combination of nitrogen-specific detector plus correct glc retention time confers considerable HCN specificity to the present evaluation.

METHODS AND MATERIALS

Apparatus. A single unit of automatic fruit sorption apparatus was used to evaluate the sorption of HCN by citrus fruits during fumigation. A schematic diagram of a unit of this essentially all-glass apparatus, previously reported by Gunther *et al.* (1958) but especially modified for this project, is reproduced in Figure 1; Figure 2 shows details of part F.

The sample chamber measured 4 × 42 in., with a volume of nearly 8 l. Rapid internal circulation of the mixture of air and HCN within the chamber was established at 350 l./min using the special circulating pump of Gunther *et al.* (1958). The pumping system was modified so that the motor ran on D.C. rather than A.C. current in order to allow operation at lower temperatures for sustained periods. The D.C. power source for the pump motor was a full-wave rectifier consisting of four diodes (Delco 5214377-6724) connected in a bridge circuit with an applied voltage of 6.3 at 10 A from a filament transformer (Chicago Standard Transformer Corp. No. P6308). An aluminum heat sink was built into the rectifier assembly to allow continuous operation.

The sample chamber D and the circulation return tube H (Figure 1) were water-jacketed for temperature control. The sample chamber contained a thermometer to check the temperature of the fruit. Water circulating in the jackets passed through a bath kept at 30° C or at 43° C. The gaseous HCN was introduced with a 100 ml gas-tight syringe through the stopcock E plus rubber nipple, and liquid HCN was in-

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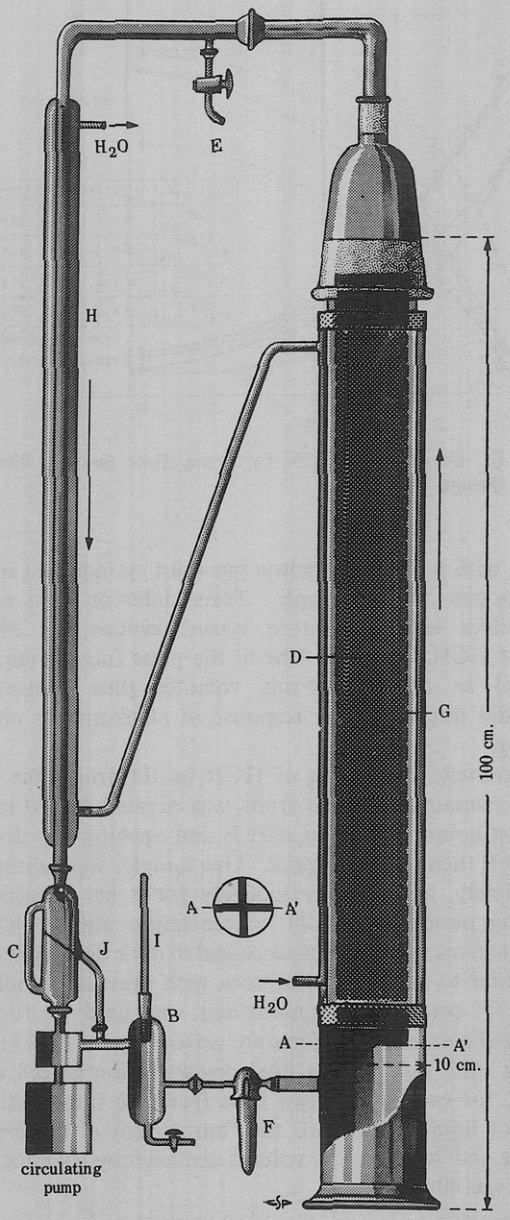


Figure 1. Automatic fruit sorption apparatus. A-A'—Glass rods to support fruits in constant-temperature, water-jacketed chamber D. B—Cyclone separator to remove oil droplets entrained in circulating pump exhaust. C—Gas-stream bypass into pump. D—Controlled temperature water-jacketed fruit chamber. E—Gas inlet stopcock and sampling port with tubing nipple. F—Ampoule breaker to introduce liquid HCN. G—Wire basket to hold fruit. H—Water-jacketed condenser. I—Thermometer. J—Capillary condensed-moisture return to gas stream

troduced by means of a special glass device F provided with a glass finger designed to break a 1-ml sealed ampoule containing a weighed quantity of liquid HCN. Fruits in the chamber were held in a wire screen basket.

A commercial metal fumatorium of 100 ft^3 capacity, equipped with a fan for providing the necessary circulation, and with temperature control system, was utilized to fumigate large amounts of fruit (Bartholomew *et al.*, 1942).

A Dohrmann gas chromatograph Model P100 equipped with a Coulson electrolytic conductivity nitrogen detector cell Model 14193, with a D.C. Bridge Model 90 and a recycling deionized water system, was used. The column was 78 × 1/8 in. o.d. stainless steel containing 80/100 mesh Porapak Q (Wilhite and Hollis, 1968), maintained at 122° C with carrier hydrogen at 125 ml/min and reactant hydrogen at 154 ml/min;

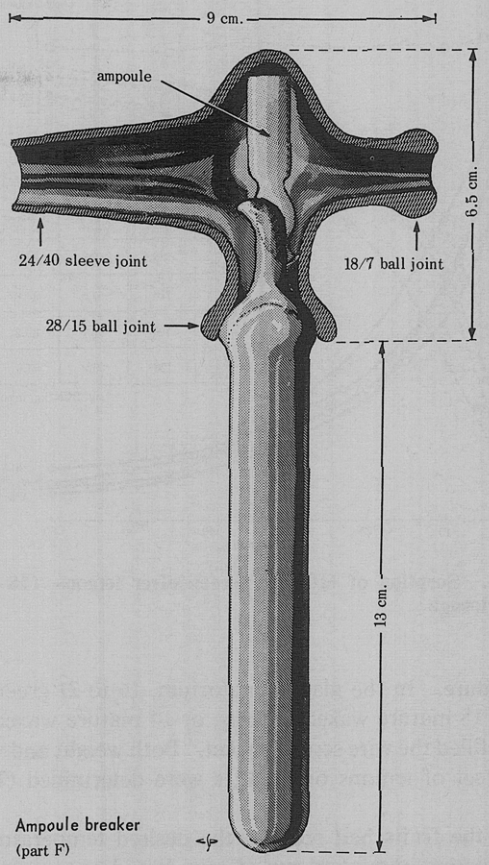


Figure 2. Ampoule breaker (see Figure 1, part F)

oven temperature was 142° C and furnace temperature was 780° C. A Carle microvolume valve No. 2014, with a 50 μl loop, was adapted to the introduction port to inject constant volumes. The retention time of HCN under these conditions was 1 min 20 sec. The linear standard curves of gaseous HCN at six different attenuations are shown in Figure 3 over the range 1.3 to 144 mg/l.

Reagents. Commercial liquid 96% HCN was obtained in 30-lb cylinders from Fumico Inc., Amarillo, Texas. Liquid HCN was drawn fresh daily from the cylinder. Liquid HCN in sealed weighed ampoules was used when high concentrations of HCN gas were necessary. Dilute gaseous HCN samples of known concentration were drawn from a 20.750-l. flask in which a sealed weighed ampoule of liquid HCN had been broken to prepare the gaseous stock solution; only the 6 mg/l. samples were obtained from this stock solution of HCN in air.

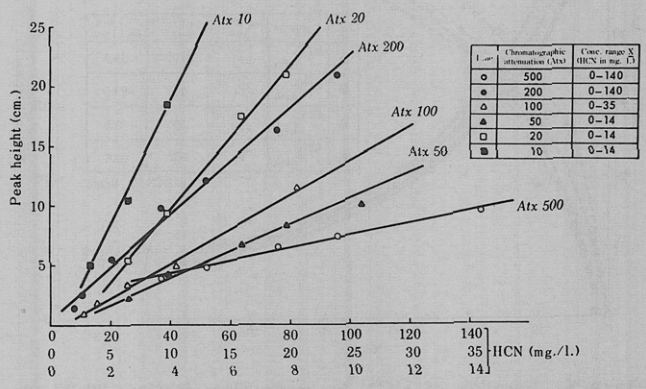
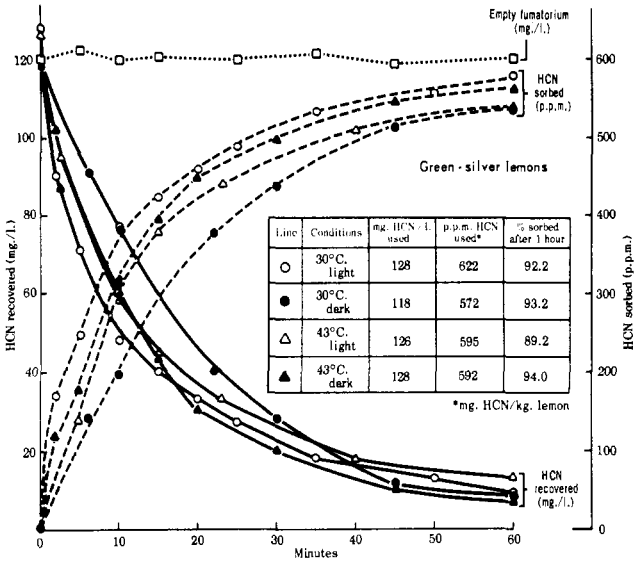


Figure 3. Standard curves of gaseous HCN at six attenuations

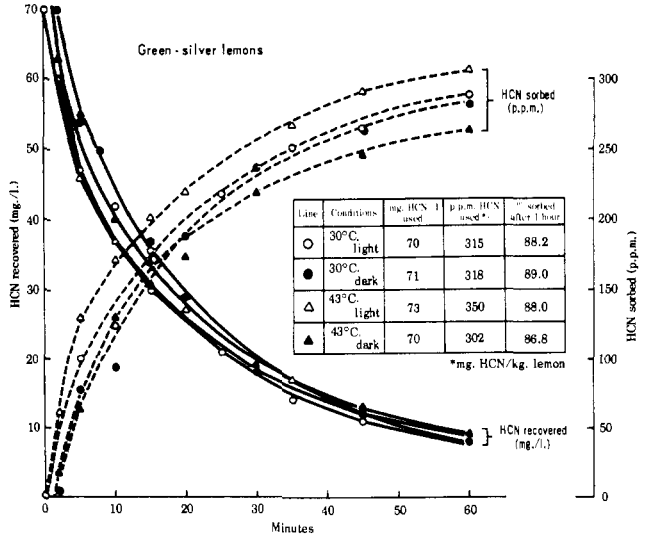


Line	Conditions	mg. HCN/l. used	p.p.m. HCN used*	% sorbed after 1 hour
○	30°C. light	128	622	92.2
●	30°C. dark	118	572	93.2
△	43°C. light	126	595	89.2
▲	43°C. dark	128	592	94.0

Figure 4. Sorption of HCN by green-silver lemons, 118–128 mg HCN/l. dosage

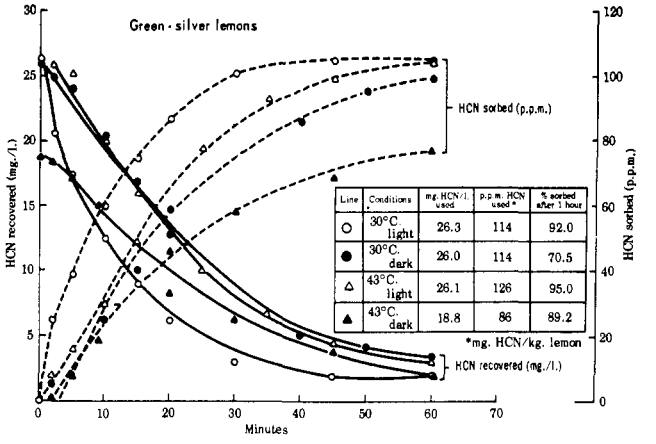
Procedure. In the glass fumatorium, 16 to 21 green-silver lemons, 18 mature waxed lemons, or 14 mature waxed navel oranges filled the wire screen basket. Both weight and volume of each set of lemons or oranges were determined (Turrell, 1946).

After the fruits had reached the desired temperature and the circulating pump had run 45 min, liquid or gaseous HCN was introduced through F or E (Figure 1). To fumigate green-silver lemons, four final concentrations of HCN (from 6 to 128 mg/l.) were used to determine what happened over a wide range of treatments. To fumigate mature waxed lemons and oranges, final concentrations of 6 and 28.8 mg of HCN/l. were used. To prepare the low concentration of 6 mg of HCN/l. 280 ml from the 20-l. flask containing 160.5 mg of HCN/l. was introduced into the gas sampler port E. To fumigate at 18.8 mg of HCN/l. or more, the appropriate weight of liquid HCN in a 1-ml sealed ampoule was placed in port F, then broken after warming the chamber F with a hot-air blower. At 2, 5, 10, 15, 20, 30, 45, and 60 min intervals, samples from the fumatorium were withdrawn at



Line	Conditions	mg. HCN/l. used	p.p.m. HCN used*	% sorbed after 1 hour
○	30°C. light	70	315	88.2
●	30°C. dark	71	318	89.0
△	43°C. light	73	350	88.0
▲	43°C. dark	70	302	86.8

Figure 5. Sorption of HCN by green-silver lemons, 70–73 mg HCN/l. dosage



Line	Conditions	mg. HCN/l. used	p.p.m. HCN used*	% sorbed after 1 hour
○	30°C. light	26.3	114	92.0
●	30°C. dark	26.0	114	70.5
△	43°C. light	26.1	126	95.0
▲	43°C. dark	18.8	86	89.2

Figure 6. Sorption of HCN by green-silver lemons, 19–26 mg HCN/l. dosage

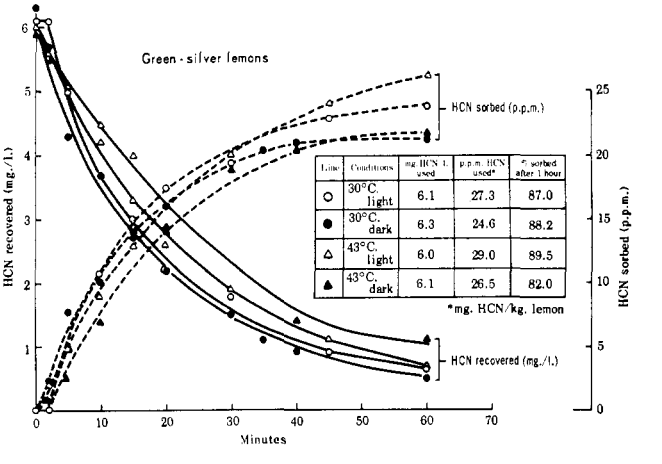
port E with a 10-ml Hamilton gas-tight syringe and injected into the gas chromatograph. Three different loads each of green-silver lemons, mature waxed lemons, or oranges, without HCN, were run 4 hr in the glass fumatorium, then sampled as controls. Fruit volatiles plus transpiration water did not cause any response at all from the nitrogen detector.

To evaluate desorption of HCN by the fruits, the fumatorium containing treated fruits was aerated for 10 min by applying house vacuum at part E and opening the stopcock on part B then resealed again. Gas samples were withdrawn immediately, and then periodically for 3 hr. During this sampling period the HCN concentration always built up from 0 to a maximum, then decreased to none detectable again.

In order to compare laboratory with practical conditions, a 100 ft^3 commercial fumatorium was used to fumigate 35 packed cartons each of mature waxed lemons (584 kg) and oranges (653 kg), with a final concentration of 5.8 mg of HCN/l. for each of the two runs from the introduction of 25 ml of liquid HCN into the fumatorium at atmospheric pressure and 70° F. The volume occupied by each lot of 35 cartons was 40 ft^3.

RESULTS AND DISCUSSION

Stability of the air-HCN standard mixture in the light and at room temperature was tested over 3 months with 128 mg of HCN/l. Small variations (±2% of average reading)



Line	Conditions	mg. HCN/l. used	p.p.m. HCN used*	% sorbed after 1 hour
○	30°C. light	6.1	27.3	87.0
●	30°C. dark	6.3	24.6	88.2
△	43°C. light	6.0	29.0	89.5
▲	43°C. dark	6.1	26.5	82.0

Figure 7. Sorption of HCN by green-silver lemons, 6 mg HCN/l. dosage

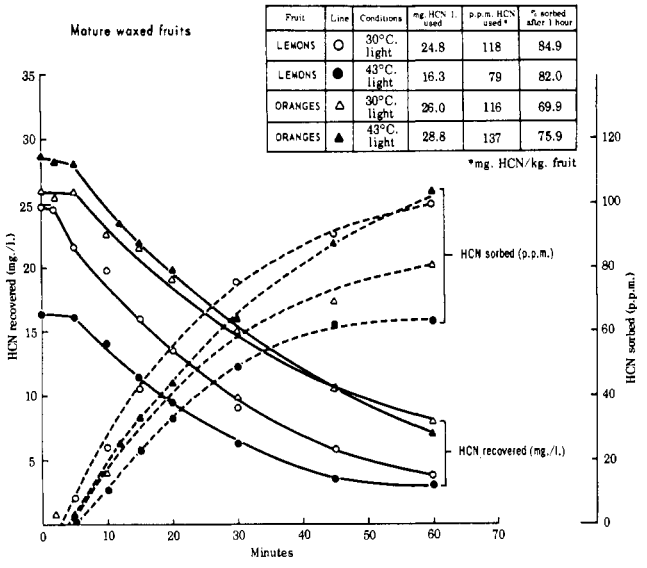


Figure 8. Sorption of HCN by mature waxed lemons and oranges, 16–29 mg HCN/l. dosage at two temperatures

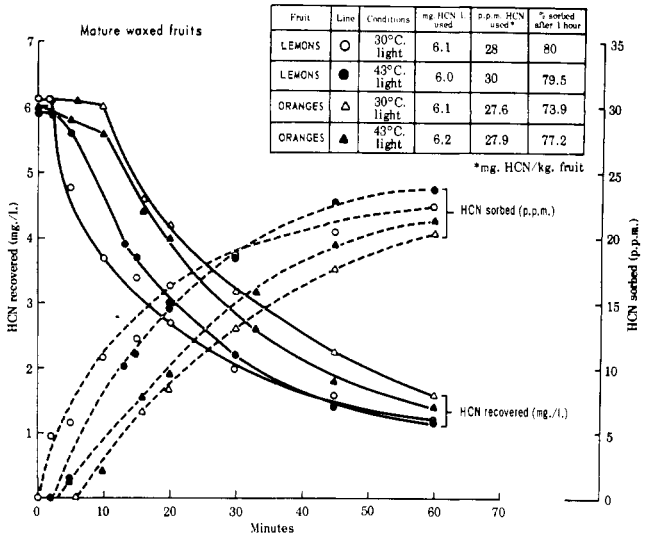


Figure 9. Sorption of HCN by mature waxed lemons and oranges, 6 mg HCN/l. dosage at two temperatures

were found for the first 60 days, with 15% drop after 90 days. Liquid HCN decomposes unless stabilized (Walker and Eldred, 1925).

Fruits were fumigated in the glass fumatorium at concentrations of HCN of from 6–128 mg/l. during 1 hr at 30° C and at 43° C both in light and in dark to establish possible effects (Bartholomew *et al.*, 1942) of temperature and light on the sorption and desorption of HCN. Six milligram/liter for 1 hr during the early morning or late afternoon are the recommended fumigation conditions for citrus fruits (Monro, 1961). In the following figures each curve represents one typical run.

Sorption of HCN by Green-Silver Lemons in the Laboratory. The sorption of gaseous HCN by green-silver lemons is shown by typical curves in Figures 4–7. The empty glass fumatorium does not sorb HCN at least during the first 60 min, as illustrated in Figure 5. The amount of gaseous HCN sorbed by the fruit during fumigation for 1 hr varies from 71 to 95% of the initial concentration. The absolute amount of HCN sorbed by the fruits varies from 22 to 572 ppm (mg of HCN/kg of whole fruit), depending on the initial concentration used. The sorption of HCN is, in general, independent of light or temperature changes from 30° to 43° C.

Desorption of HCN by Green-Silver Lemons in the Laboratory. The purpose of this experiment was to establish how much and how fast HCN is desorbed by the fruit after 10 min aeration, and how long it takes to resorb the HCN thus reintroduced into the fumatorium. Results, summarized in Table I, indicate that from 3 to 7% of the HCN previously sorbed by the lemons desorbed after aeration for 10 min. In other terms, 10–21 ppm of HCN was desorbed by these fruits, depending on the initial HCN concentration and the fumigation conditions. The absolute desorption reached maximum after about 45 min, and subsequent resorption was complete in 85 min.

Table I. Percent HCN Desorbed[a] by Green-Silver Lemons in the Laboratory

Time (min)	Light and 30° C	Dark and 30° C	Light and 43° C	Dark and 43° C
0	...	...	...	...
10	...	3.0	3.2	...
15	4.9	4.2	...	4.4
30	6.0	...	...	4.9
45	7.4	...	...	...
60	...	4.3	...	...
85	ND[b]	ND[b]	ND[b]	ND[b]

[a] After 10 min of aeration. [b] ND none detectable.

Sorption of HCN by Mature Waxed Lemons and Oranges in the Laboratory. Mature waxed Eureka lemons and navel oranges were fumigated in the all-glass apparatus in light and in dark at 30° and 43° C, with the amounts of HCN shown in Figures 8 and 9. Sorption of HCN varied for lemons from 80 to 84% and for oranges from 70 to 77% of the initial amount after 1 hr of fumigation, or 23 to 100 ppm sorbed by these lemons and 20 to 102 ppm sorbed by these oranges in a 1 hr fumigation. The wax on the fruit prevented immediate sorption, as shown by the maintenance of the initial concentration for the first 5–10 min following initial exposure. After this induction period the sorption curves resemble those for unwaxed fruits.

Sorption of HCN by Mature Waxed Lemons and Oranges in a Commercial Fumatorium. Thirty-five boxes (584 kg) of Eureka lemons and 35 boxes (653 kg) of navel oranges were fumigated at 70° F and at atmospheric pressure with 5.8 mg

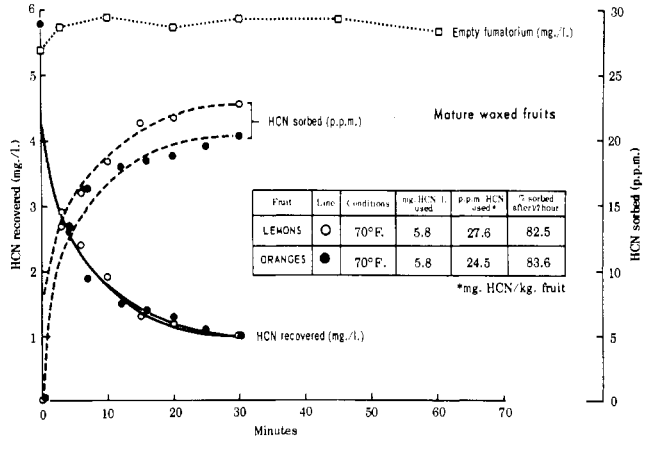


Figure 10. Sorption of HCN by mature waxed lemons and oranges in a commercial fumatorium, 6 mg HCN/l. dosage and 70° F

Table II. HCN Residues Retained by Fumigated Lemons and Oranges

Maturity and Variety	Waxed or Unwaxed	Fumatorium	Dosage (mg/l)	Residue in Fruit (ppm)
Green-silver lemons	Unwaxed	Laboratory	6	22–26
			19–26	78–120
			70–73	263–308
			118–128	532–572
Mature lemons	Waxed	Laboratory	6	22–24
			16–25	65–100
		Commercial	6	23
Mature oranges	Waxed	Laboratory	6	21–22
			16–25	81–100
		Commercial	6	21

of HCN/l. for 1 hr, with results shown in Figure 10. Under these conditions the sorption took place rapidly, and in 30 min 83% of the initial concentration of HCN was sorbed by the lemons and 84% was sorbed by the oranges. The empty fumatorium did not sorb HCN during 1 hr, as shown in Figure 10.

Residues of HCN in the Fumigated Fruit. Table II represents a summation of the residues of HCN actually retained by the fumigated Eureka lemons and navel oranges for the dosages utilized. The higher residues clearly could be expected in fruits close to the point of introduction of the HCN in a commercial fumigation. As pointed out earlier, only 3–7% of these residues was desorbed, even upon prolonged aeration. Bartholomew *et al.* (1939, 1942) found that 72 to 85% of the HCN sorbed by Valencia oranges was fixed in the orange tissues after 48 hr; the present data indicate even faster conversion to nondesorbable HCN residues.

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LITERATURE CITED

Bartholomew, E. T., Sinclair, W. B., Jones, B. F., *Hilgardia* **12,** 473 (1939).
Bartholomew, E. T., Sinclair, W. B., Lindgren, D. L., *Hilgardia* **14,** 373 (1942).
Gunther, F. A., Blinn, R. C., Kolbezen, M. J., Wilson, C. W., Conkin, R. A., *Anal. Chem.* **30,** 1089 (1958).
Lindgren, D. L., Vincent, L. E., *Advan. Pest Contr. Res.* **5,** 85 (1966).
Monro, H. A. U., "Manual of Fumigation for Insect Control," F.A.O., Rome, 1961.
Moore, W., Willaman, J. J., *J. Agr. Res. XI,* 319 (1917).
Turrell, F. M., "Tables of Surfaces and Volumes of Spheres and of Prolate and Oblate Spheroids and Spheroidal Coefficients," First Ed., Univ. of Calif. Press, Berkeley, 1946.
Walker, M., Eldred, D. N., "The Decomposition of Liquid Hydrocyanic Acid," The Pacific R & H Chemical Corporation, El Monte, Calif., 1925.
Wilhite, W. F., Hollis, O. L., *J. Gas Chromatogr.* **6,** 84 (1968).

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